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DIELECTRIC STUDY OF ESTERS: ELECTRIC DIPOLE MOMENTS AND MOLECULAR CONFIGURATION

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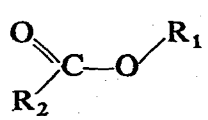
ABSTRACT

Electric dipole moments of ethyl isobutyrate, ethyl cyanoacetate, dibutyl *o*-phthalate, and diethyl butylmalonate (diethyl 2-*n*-butyl-propanedioate) in benzene solution and those of phenyl acetate and ethyl bromoacetate in carbon tetrachloride solution have been determined at 30 °C, using Halverstadt–Kumler's standard method. The moments of these esters have also been calculated theoretically and the results interpreted in terms of their molecular configuration.

INTRODUCTION

Many esters derived from the saturated monohydric alcohols and saturated carboxylic acids have been found to possess a rigid *trans*-planar configuration and the electric dipole moments of these esters are independent of temperature[1]. However, methyl and ethyl chloroformates and carbonates are exceptions and restricted rotation of OR_1 about the C–O bond has been suggested to account for this[2].



In previous work reported from this laboratory[3,4], these ester molecules have been shown to possess a configuration in which the C–O–C plane lies considerably out of the *trans*-plane and the possibility of intramolecular rotation or rotatory oscillation about the position of minimum potential energy is expected, which is in accordance with the findings of electron diffraction studies[5]. The presence of intramolecular rotation often results in an increase in the electric dipole moment of the molecule. The present investigations have been carried out to study the configuration of some of the esters in the light of the above view-points.

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EXPERIMENTAL

The measurement of the dielectric constants and densities of the solutions has been described elsewhere[6,7]. Halverstadt and Kumler's standard method[8] was employed for the evaluation of electric dipole moments. The constants α, β, ε_1, and v_1 appearing in the rectilinear expressions governing the variations of dielectric constants and specific volumes with the change of concentration (at low range), were evaluated by the method of least squares. The distortion polarization ($P_e + P_a$) has been taken to be the same as the molar refraction values for the sodium-D line.

The solvents benzene (S. Merck, G. R.) and carbon tetrachloride (E. Merck, G. R.) were distilled and the fractions boiling at 79 °C and 75 °C respectively, were collected and kept in a desiccator before use. Ethyl isobutyrate (Fluka, Switzerland), phenyl acetate (B.D.H., England), ethyl bromoacetate (Fluka, Switzerland) and ethyl cyanoacetate (Boehringer, Ingelheim, Germany) were distilled, and the fractions boiling at 111 °C, 195 °C, 159 °C and 205 °C respectively, were collected and used. Fresh samples of dibutyl *o*-phthalate (Naarden, Holland) and diethyl butylmalonate (Riedel, Germany) were employed without further purification.

TABLE 1

EXPERIMENTAL PARAMETERS AND ELECTRIC DIPOLE MOMENTS OF ESTERS

Temperature 30 °C; the concentration range of the solutes used in these investigations was 0.01 to 0.08 by weig fraction. The dielectric constants and specific volumes were found to vary linearly with concentration. The u certainty in the determination of the slopes (α and β) and the moment value is ±1 %.

No.	*Compound*	*Solvent*	α	β	$P_{2\infty}{}^{a}$(*ml*)	$\mu_{obs.}$(*D*)	$\mu_{calc.}$(*D*)	$\mu_{lit.}$(
1	Phenyl acetate	Carbon tetrachloride	4.39	0.30	100.8	1.78	1.6^{b} 1.8^{c}	1.65 (ref. 1
2	Ethyl bromoacetate	Carbon tetrachloride	6.95	0.14	148.6	2.43	1.78^{b} 2.40^{c}	2.42 (ref.
3	Ethyl isobutyrate	Benzene	2.75	0.01	100.3	1.84	1.6^{b} 1.8^{c}	2.07 (ref. 9
4	Ethyl cyanoacetate	Benzene	15.26	−0.39	354.6	4.04	3.14^{b} 3.90^{c}	—
5	Dibutyl *o*-phthalate	Benzene	3.06	−0.19	239.8	2.85	3.17^{d}	—
6	Diethyl butylmalonate (diethyl 2-*n*-butyl-propanedioate)	Benzene	2.96	−0.12	187.3	2.55	—	—

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[a] $P_{2\infty}$ is the molecular polarization at infinite dilution.

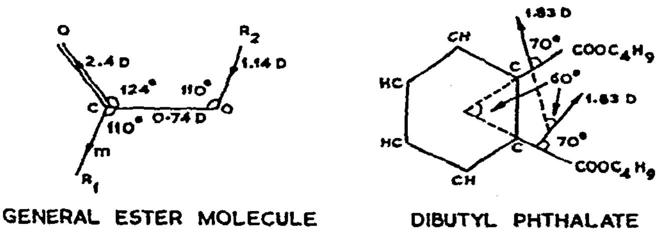
[b] Calculated by assuming rigid *trans*-planar model.

[c] Calculated by assuming C–O–C plane 30° out of the *trans*-plane.

[d] Resultant group-vector moment.

RESULTS AND DISCUSSION

The experimentally determined parameters ($P_{2\infty}$, α and β), the observed and the calculated electric dipole moments, along with the literature values available for some of the esters are summarized in Table 1. Theoretical calculations of the molecular moments have been made on the lines suggested by Smyth[12], assuming the molecular models shown in Fig. 1. The magnitudes of the parameters employed for the calculation are the same as given by Smyth[13].



GENERAL ESTER MOLECULE DIBUTYL PHTHALATE

Fig. 1. Models of ester molecules. $R_1 = CH_3$, CH_2Br, $(CH_3)_2CH$ and CH_2CN for esters 1, 2, 3 and 4 respectively in Table 1. $R_2 = C_2H_5$ for esters 2, 3, 4, and C_6H_5 for ester 1 in Table 1. $m = -0.4$ D for esters 1 and 3, 1.8 D for ester 2 and 3.4 D for ester 4 in Table 1.

For the first four esters in Table 1, a comparison of the observed and calculated electric dipole moments indicates that these molecules possess a configuration in which the C–O–C plane lies 30° or more out of the *trans*-plane, which is supported by electron diffraction studies of some esters[5]. The possibility of intramolecular rotation or rotatory oscillation about the position of minimum potential energy may cause a slight difference in moments with the variation of the experimental conditions. This may be one of the reasons for the difference of the present moment values of some esters from the values reported in the literature. The comparatively higher observed moment of ethyl cyanoacetate is attributed to the inductive as well as the resonating polar structures of the cyanide group[14].

The observed moment for dibutyl *o*-phthalate is lower than calculated by group moment vector addition. This decrease is expected to be due to the well-known *ortho*-effect, in which two identical groups placed adjacent to each other repel one another and lead to a widening of the angle of inclination between the two moment vectors, resulting in a decrease of the overall moment[15]. The lower electric dipole moments reported for dimethyl *o*-phthalate (2.80 D)[16] and diethyl *o*-phthalate (2.80 D)[17] than the calculated moment (3.17 D), indicate a similar effect. In diethyl butylmalonate (diethyl 2-*n*-butyl-propanedioate), the two $-COOC_2H_5$ groups are free to rotate relative to one another. The mean moment for such a case is 2.69 D[18] which, being close to the observed dipole moment for diethyl butylmalonate, indicates the presence of intramolecular rotation in this molecule. If we assume that the addition of alkyl groups does not appreciably change the moments, our observed value for diethyl butylmalonate is in good agreement with the moment for diethyl malonate (2.56 D)[19].

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